THE NONTOXIC WATERY SOLUTION AGAINST FREEZING AND CORROSION AND THE REGENERATOR FOR THE UTILIZED ANTIFREEZE

THE FORMULATION OF NONTOXIC LIQUID WATERY SOLUTION AGAINST FREEZING AND CORROSION

THE ESSENCE AND DECRIPTION OF INVENTION

The invention provides that nontoxic cooling liquid (anti-ice/ antifreeze) designed on nontoxic base in aqueous solution, till 96% concentration, could be automatically usable. This cooler could be usable as concentrated or diluted with distilled water. It's applicable instantly. The invention is new (new technology), resourceful and applicable on the day of patent protection application. It's nonpoisonous and nontoxic.

Note: Inventions The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion and The Formulation of Watery Solution of Inhibitor Against Corrosion for Utilized Antifreeze are depended on each other regarding their parts, but they are applicable in their innovated procedures and as two separated technology. The invention The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion is a new technology with the substances which can be applicable in a production and in a cooling systems with the inhibitors composition in a direct usage as it has been described in an invention, or with a finished invention The Formulation of Watery Solution of Inhibitor Against Corrosion for Utilized Antifreeze, also described and has its usage. It is also instantly applicable in a production and cooling systems and it's resourceful.

THE COMPERATIVE ADVANTAGE OF INVENTIONS *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion* AND *The Formulation of Watery Solution of Inhibitor Against Corrosion for Utilized Antifreeze:*

Inventions *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion* and *The Formulation of Watery Solution of Inhibitor Against Corrosion for Utilized Antifreeze* are NONTOXIC LIQUID, biodegradable, and are not harmful for the environment, water, nature, human health, animals, pats and fishes.

Formulation of the watery solution against freezing and anticorrosive protection in cooling and heating systems

This invention is in the field of cooling the internal combustion engines (passenger and truck vehicles), other systems of cooling and heating where the heat exchanger is used. More precisely, it's in the field of fluid – liquid for the cooling of engines. According to international patent classification the invention is assorted in class C 09 K 005/00, by which the equipages and gadgets on vehicles are defined for the remission of cooling the machinery units by cooling liquid. The invention could be also assorted in class F 01 P 3/00 or in class V60K 11/02 by which the cooling of engine in general is defined, that is, cooling by cooling liquids.

This invention has been done on nontoxic base.

That's why it's called Invention for 21st Century New technology

THE SOLUTION OF THE TECHNICAL PROBLEM OF THE INVENTION

The solution of the problem is how to produce an agent against freezing and boiling in open and closed systems of cooling so, by the application of the procedure, the nontoxic liquid (fluid) for the heat exchange could be achieved, as well as to achieve an anticorrosive protection for all the metals in system, especially for the aluminum engines or parts of the engines. By application of this procedure in invention *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion,* by mixing of distilled – soften water, nontoxic base (glycerol), prepared inhibitors (at least 17 substances) mixed in one and other additives, the agent for engine cooling has been achieved, which will be ecological correct, biodegradable, nontoxic and it's not harmful to the natural resources, doesn't pollute land and water, and it's not toxic to the people, fishes, animals and pets, and besides, successfully protects engine (system from freezing and corrosion, from formation of stone and foam in system, while the boiling point upraises over 120°C). The most important fact is that it doesn't endanger and not poisoning a driver during driving, other passengers, and so it has an influence on the safety in a traffic. The other fluids (antifreezes) are carcinogenic.

STATE OF TECHNIQUE AND MARKET

There are cooling fluids which are used in the systems of cooling in internal combustion engines in open and closed systems, and doesn't freeze till the temperature from –30°C to –40°C. The most of this fluids are sold by the term Antifreeze, and the Producers in Serbia and Montenegro are: Kotrman, NIS Naftagas, Petrohemija Pančevo, in Bosnia: Optima Modriča and others, and in the world: BASF Germany, Preston America, etc.

According to our information, collected in the last ten years, through internet and other electronic media and other information, none of the antifreezes hasn't been done on NONTOXIC base and doesn't have such a certification that it's not toxic, biodegradable, and that it doesn't pollute environment, and the technical solution has been designed on the very high level regarding anticorrosive protection of engines as well as the durability.

The defect of mentioned solutions is in the fact that they are toxic, life-time is limited on two years, insufficient inhibitor protection, poor alkali reserve, low pH value about 6.2-7.2, and it should be between 9.5-11.5 according to ASTM. This invention completely meets ASTM standards.

THE COMPARATIVE ADVANTAGE

The mentioned above inventions (aqueous fluid diluted with distilled water) and as fluid concentrate in cooling systems, are consists of the following:

Cooling liquid is NONTOXIC, biodegradable, nonpoisonous and doesn't pollute environment. It's durable in cooling system (over 6 years) or 350.000 km. Temperature in minus till –70°C, depends of the concentration, concentration till 96%. The

advantage of this patent is also in persistence of high temperature, in plus till 160°C. Traditional cooling fluids – antifreezes with all trade names has been done on traditional base TOXIC one, mono-ethylene glycol or other glycol bases. For this invention of fluid solution there is no need for the any precautionary measures during usage and changing in engine systems. For the all other antifreezes there is an obligation of warning by law that it's TOXIC.

THE ESSENCE OF THE INVENTION

The technical problem is successfully solved by the manufacturing process of *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion* first of all in open and closed systems of cooling. According to this invention application, the process is performed in several phases.

First there is mixing of distilled water (soften till I level)or totally distilled, free of all minerals and pollutions with glycerol (multivalent alcohol) on 80-90°C, with constant mixing till homogenization. The ratio of a basic substance can be different,(66:34, 70:30, 80:20) it all depends of what we want to design. In ratios mentioned above it's necessary to leave a space for the inhibitor from the Formulation *The Formulation of Watery Solution of Inhibitor Against Corrosion for Utilized Antifreeze* in a quantity participation of 10-20%, and then there is a continuance with heating on the same temperature and mixing till the total homogenization of product. Against the foam, the silicate oil in small concentration of 0,004-0,009% is mostly added. Beside that, the color of high quality and also nontoxic is added, which is used in food or cosmetics. The final product is light-green liquid or heavenly blue. There is a need for adding the color in fluid so we can know that there is a liquid in the system, because, the liquid obtained on this way has white transparent color.

Besides this invention process with adding the inhibitor which is a formulation of aqueous solution of corrosion inhibitor under *The Formulation of Watery Solution of Inhibitor against corrosion for utilized antifreeze* or marked in formulation under A and B, as a explanations of detailed formulation. The problem of inhibitor protection for all the engines in which this fluid is used, is solved by usage of inhibitor which is an integral part in formulation of invention *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion.* In this way, the problem of the engine anticorrosive protection is completely solved. In this way, the nontoxic antifreeze (invention *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion*) exploitation process is enriched in all the engine systems of cooling and heating and other systems of cooling and heating.

The product obtained by this process is modified and improved with anticorrosive protection for all engines, and specially an aluminum engines and other contact metals, achieves anticorrosive protection.

The product obtained by this process, can be concentrated liquid – aqueous solution with dilution before usage according to a manufacturer instruction, as well as the aqueous solution without diluting before usage.

The invention obtained by this process is intended for open and closed systems for cooling of engine SUS, and also can be used in other systems for the heat transmission with liquid circulation, as well as the transformer of cooling and heating. This liquid is suitable for the protection of all systems from freezing and boiling.

Especially its usage can be in food industry and nonalcoholic and alcoholic drinks industry, because, if some system damage occurs and leaking of fluid from the system, there is no danger of poising or pollution of products, as well as the environment pollution.

THE COMPARATIVE ADVANTAGE OF THIS INVENTION IN REGARD TO THE TRADITIONAL ONES:

The fluid – antifreeze, according to this process is NONTOXIC SUBSTANCE.

Nonpoisonous is characterized in fact that it has been done on basic base of multivalent alcohol.

The main advantage of the nontoxic fluid – antifreeze on the base of multivalent alcohol (glycerol) is that the glycerol, as a dominant component, is a natural product, in contrast to other fluids against freezing, which have, as an active component, synthetic compounds – xeno-byotics, such as ethylene, propylene – glycol and mono-ethylene glycol. Nonpoisonous is confirmed by the State Institute Bavaria in Germany, as well as by analyses from the Institute in Belgrade – NU Institute for chemistry, technology and metallurgy – center for chemistry in Belgrade. This analyses proves that this patented fluid is nontoxic, nonpoisonous and doesn't pollute an environment. The materials used for the reducing of foam and corrosion must be totally disintegrated in this product and mutually compatible. This materials, as well as the fluid itself, mustn't make sediment, be separated from the fluid or to make chemical negative reaction between them.

Something more about corrosive protection of nontoxic invention fluid:

Anticorrosive protection in chemical heterogenous effect has been given in average power of anticorrosive protection, keeping in mind that cooling liquid in the function of engine cooling effects on several metals, also heterogenous composition.

The inhibitor's anticorrosive protection is the solution for the modified and synthesized protection from corrosion and damage of whole cooling system of all engines, of course, beside specific and mentioned metals, it protects rubber, plastic and other hoses, asbestos, teflone parts and other gaskets, too. The inhibitor is a subject of a new technology, marked as an invention *The Formulation of Watery Solution of Inhibitor Against Corrosion for Utilized Antifreeze.*

Regarding the fact that the engine systems consists of several different elements, above all, copper, 2006 solder, brass, soft steel, iron and aluminum (there is increasing usage of aluminum for the modern engines), so this invention is on the base of multi-atomicity alcohol (glycerol) and has inhibitor protection by which we obtain the balance of protection of all metal elements used for the engine cooling system construction.

The advantage of the invention is that very high boiling point is achieved, depends of the basic concentration (glycerin), till 96%, for example, 120°C-162°C in plus, and in minus from –40°C till –70°C. One more advantage of the invention is that if low temperature occurs, this fluid doesn't transfer into solid aggregate condition, but in dilapidated crystals which doesn't do any pressure on the engine walls, hoses and other, but it realizes them, and during the starting of engine they easy get warmer and start to melt without any damage of the engine and other parts of the cooling system.

The Formulation of inhibitors for the invention *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion*

A) Additives as inhibitors

1. Glycerol
- chemical formula $C_3H_8O_3$
- quality min. 98,0% (99,5%)

2. Water – soften or distilled

3. Benzotriazole – effective inhibitor against corrosion of metals in neutral solutions

4. Three-ethanol-amine $(HOCH_2CH_2)_3N$ – an inhibitor against corrosion of iron and steel in watery solution)

5. Sodium-tetraborate
- chemical formula $Na_2B_4O_7$
- an inhibitor for several metals, aluminium and their alloys

6. Sodium-nitrate
- chemical formula $NaNO_3$
- protects several metals

7. Sodium-nitrite
-chemical formula $NaNO_2$
-necessary concentration depends on corrosion conditions and water content in formulation

8. Sodium-sulfide
- chemical formula (without water $NaSO_3$) or $(naSO_3)_7H_2O$
- in this formulation, it's a good inhibitor for magnesium, aluminum or their alloys in alkali environment or in watery solution of glycerol

9. Potassium-sulfide
- chemical formula K_2SO_4
- min. 99% quality
- solution-easy soluble in water
- in this formulation, an inhibitor of aluminum, magnesium and their alloys

10. Sodium-chromate
- chemical formula in acids HNO_3, H_3PO_4 and H_2SO_4
- corrosion inhibitor of steel, cast iron, aluminum, cooper, zink and messing in watery solution of this formulation

11. Sodium-benzoate

- chemical formula $C_6H_5SO_6Na$ or ($C_7H_5O_2Na$)
- corrosion inhibitor of steel in watery solutions and well preserved pH value and alkalis

12. Calcium-cyanamide
- in this formulation, corrosion inhibitor of steel in watery solutions and solutions of salts

13. Sodium-hydroxide
- suitable for aluminum protection as well as for the preserving of alkali reserve and pH value between 9-11

14. Polymark-polycaroxilate BASF, soluble in watery and alcohol solutions. In this invention is marked as SOKALON® CP-12S or CP-10. In this formulation well applicable is ABC COBLEX's polycarboxilate, too.

15. Sodium-metaborate
- chemical formula (calculated on B2O3)+2+3+4 with application in concentration 0,5-5 mass parts
- an inhibitor for metals in formulation of nontoxic antifreeze based on glycerol

TABLE "A"

FORMULATION	A	B	C	D
Components u %	(range	of formulation	additives)	
A)				
- distilled water	32,40	24,00	24,00	25,00
- three-ethanol-amine	0,60	1,00	3,10	3,60
- poly-carboxilate	0,60	1,00	2,60	3,40
- benzotriazole	0,50	1,50	3,20	4,80
B)				
- distilled water	55,00	48,00	39,00	33,00
- sodium-tetraborate	0,20	0,40	0,60	0,80
- sodium-nitrate	0,20	0,30	0,40	0,45
- sodium-nitrite	0,15	0,25	0,35	0,45
- sodium-sulfide	0,10	0,25	1,10	1,40
- potassium-sulfide	0,13	0,90	2,20	2,90
- sodium-chromate	0,10	0,20	0,65	1,00
- sodium-benzoate	0,10	0,20	0,35	0,45
- sodium-hydroxide	0,03	0,05	0,08	0,10
C)				
- distilled water	10,00	20,00	19,00	20,00
- sodium-metaborate	0,20	0,30	0,40	0,80
- calcium-cyanamide	0,20	0,35	0,45	0,90
- silicon oil	0,005	0,005	0,005	0,005

In all the variants the basic substance participates between 48% and 88%. This fluid depends of the climate and other conditions of production and usage, how and where it will be designed. It's anticipated from –15°C till –70°C and from 110°C till 170°C.

If we are dealing with the preparation of liquid against freezing and corrosion, this technological process is applied, and if it's about the inhibitor who has been already prepared for this kind of product, the procedure is as follows: there is a mixing of basic substance with water and then the inhibitor is added in quantity 8-15% of mass weight, and then there is a mixing by given procedure.

For the liquid against freezing and corrosion in engine cooling systems, the performing of the production process is the following:

The substances-additives in group A is mixing, then, there is a mixing of additives from group B, and finally, the mixing of additives from group C. After that, on the same sequence as above, there is mixing of groups, one by one, on the temperature of 80°C, using a mixer with small numbers of revolutions, about 100-200 revolutions per minute.

The mixed additives are mixing into the basic substance, according to tables and sequence, after the preparation of additives. The relations is the following: for minus temperature of –25°C, the additives from table "A" are used with 38% of basic substance, for temperature of –35°C, the formulation from table "A"/B is mixing with 48% of basic substance, for temperature of –55°C the formulation from table "A"/C is mixing with the 60% of basic substance, and for the minus temperature over –65°C there is a mixing of formulation from table "A"/D with the 88% of basic substance. All these combination can maintain the temperature from 110°C till 160°C in plus.

After that, the product is filled into the package according to market and producers wish, and patent's product is ready to be applicable immediately.

This is the nontoxic liquid-fluid anti-ice, which shouldn't be marked as toxic.

CONCLUSION

Beside the mentioned inhibitors, mono carbonic acid and polycarboxylate in small concentration are very suitable for the corrosion inhibition of all various kind of engines. There are also azole compounds, suitable to this invention, including mercaptobenzothiazole, benzothiazole and poly-three-azole salts. The best are salts of nitrite and nitrate and their mixture. Phosphates can also be useful for the corrosion inhibition.

For this invention, formulation of aqueous solution or concentrate, engine cooler or anti-ice, some of most suitable inhibitors were selected with well balanced inhibition, and protection for all kind of metals had been done. This technology has been done after intensive examination, and excellent results are obtained regarding protection of all mentioned kinds of metal.

The formulation is perfectly selected (review given in tables) so the balance is obtained on this base of aqueous engine cooler, as well as the concentrate.

The invention is finally attested by modified method in three X three method ASTM and DIN, using DIN method which has been used to estimate the invention

formulation against corrosion. Beside that, corrosion standard test method on engine cooler in glass can with corrosive solution, has been used, too.

Invention examination by author is finished with this, and comparison with other conventional product for engine cooling, as well.

The result is: this is completely new technology ("new technology") and it hasn't been patented in the world till now.

The basic and the main goal of this invention is that it's: nontoxic, well disintegrating in water (biodegradable), ecological acceptable because it's not harmful to the environment and it doesn't pollute land, air and water. At the same time it's technological-technically improved, so it's useable in all cooling systems (cars), heating systems and in all heat transfer systems, as well as in the solar systems.

The inventions *The Formulation of Nontoxic Liquid watery Solution Against Freezing and Corrosion* and *The Formulation of Watery Solution of Inhibitor Against Corrosion for Utilized Antifreeze* are designed and consisted of different chemical substances, so now, they make two depended integers. The first one is without inhibition protection, and the second one is an inhibition protection for the first formulation and for the formulation of the utilized fluid liquids in cooling and heating systems and in internal combustion engines.

The modified version of ASTM D-1384-87 has been used to evaluate the formulation of invention. ASTM is a standard test – method for testing of corrosion in engine coolers in glass can.

ASTM presents real operating conditions of all liquids for cooling systems.

TECHNICAL REPORT

With this formulation the tests had been and the cleaning procedure of metal sample had been performed by modified ASTM specification.

With prescribed temperature, 30-33% ASTM corrosive water. All the modifications are measured in milligrams corresponding to a standards.

Table 1

	allowed	obtained by measuring
cooper	5	-0.8
solder	10	+0.6
brass	10	-0.6
iron	5	+0.2
gray smelting	5	-2.4
aluminum	10	-5.0

The results from table 1 obtained by ASTM method are passing.

Analogue examination of corrosion

Corrosion: losses in weight of archetype coupons (mostly mg)

Table 2

	allowed	obtained by measuring
copper	5	-0.6
solder	10	+0.1
brass	10	-0.6
iron	5	+0.1
gray smelting	5	-2.3
aluminum	10	-5.9

The results are obtained by modified ASTM method. The results are passing.

Corrosion: losses in weight of archetype coupons, mostly mg (JUS H.Z8.O56)

Table 3

	allowed	obtained by measuring
copper	5	+1.9
solder	10	+1.8
brass	10	+2.7
iron	5	+3.4
gray smelting	5	+3.7
aluminum	10	+4.0

the results are obtained by analogue method according to JUS HZ8.O56 in glass can with corrosive liquid 30%, and antifreeze 1:1 for the temperature of –18°C PASS.

Analyses reviews

Which have been done in order to examine an anticorrosive protection, in better words a corrosion holder – nontoxic fluid/antifreeze, invention *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion*, performed with an inhibitor, invention *The Formulation of Watery Solution of Inhibitor Against Corrosion for Utilized Antifreeze*, as an additive for utilized fluid/antifreeze.

1. the examination by University in Novi Sad, Technical Science Faculty, a laboratory for physical-technical and solar measuring in 1988 and 1989. The results correspond to JUS, ASTM and DIN standards.
2. the extreme exploitation examinations has been performed for this formulation of nontoxic fluid/antifreeze, in such a way that archetype coupons was cleaned according to ASTM method and specification. The archetype coupons were build in cooling system of General Motors's engines: Pontiac 2.300 cc, Pontiac 3.100 cc from 1991., Chevrolet Corsica 3.100 KW and Beretta 2.300 cc from 1991. The archetype coupons were used in exploitation of vehicle during summer and winter period on the temperature from –15°C till +35°C to 40°C. With such an examination between 5.000-20.000 km were passed, on the base of regular everyday drive.

On the base of this examination, the results in Tables 4,5,6 and 7 were obtained.

Table 4, Corsica 3100 cc, passed 7.000 km; Table 5, Beretta 2300cc, passed 5.000 km; Table 6, Pontiac 2300 cc, passed 10.000 km; Table 7, Pontiac 3100cc passed 20.000 km. In all the vehicles the archetype coupons were built in for 8 months. The archetype coupons were built in cooling system on the highest gavitation pressure. For example, a working pressure of a water pump is about 1 kPa. Average working temperature in engine is about +110°C. After taking off, an archetype coupons were processed according to ASTM standard.

Achieved results shows that nontoxic fluid/antifreeze, invention *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion*, with an inhibitor, invention *The Formulation of Watery Solution of Inhibitor Against Corrosion for Utilized Antifreeze*, meets high ASTM standard and it's a sufficient guarantee for all the engines in which this invention, nontoxic fluid/antifreeze is putting in a engine cooling system, and not only during the warranty period, but over 300.000 km or 6 years of engine exploitation.

Exploitation method

Table 4

	allowed	obtained by measuring
cooper	5	-1.2
solder	10	-2.4
brass	10	-0.2
iron	5	+0.6
gray smelting	5	+3.4
aluminum	10	+3.7

Table 5

	allowed	obtained by measuring
cooper	5	+1.2
solder	10	-2.3
brass	10	-2.4
iron	5	+0.4
gray smelting	5	-5.7
aluminum	10	+4.8

Table 6

	allowed	obtained by measuring
cooper	5	+2.4
solder	10	-0.5
brass	10	+0.6
iron	5	+1.4
gray smelting	5	+3.6
aluminum	10	+6.1

Table 7

	allowed	obtained by measuring
cooper	5	+1.9
solder	10	+1.8
brass	10	+2.0
iron	5	+8.6
gray smelting	5	+6.1
aluminum	10	+3.6

All the results meets a standards.

THE FORMULATION OF WATERY SOLUTION OF INHIBITOR AGAINST CORROSION FOR UTILIZED ANTIFREEZE (INHIBITOR AND REGENERATOR)

THE ESSENCE AND DECRIPTION OF INVENTION

This invention provides liquid concentrated anticorrosive formulation, suitable as an additive to the utilized fluid, antifreeze in engine cooling system. This invention, *The Formulation of watery Solution of Inhibitor Against Corrosion for Utilized Antifreeze* provides extended life-time of the anticorrosive protection to fluid/antifreeze in internal combustion engine cooling system. Considering its inhibitor characteristics it has great protection power from corrosion. This agent is used as an emulsion and modifier and in the same time it's a main anticorrosive protection in invention *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion.*

Note:

Inventions *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion* and *The Formulation of Watery Solution of Inhibitor Against Corrosion for Utilized Antifreeze* are depended on each other regarding their parts, but they are applicable in their innovated procedures and as two separated technologies. The invention *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion* is a new technology with the substances which can be applicable in a production and in a cooling systems with the inhibitors composition in a direct usage as it has been described in an invention, or with a finished invention *The Formulation of Watery Solution of Inhibitor Against Corrosion for Utilized Antifreeze*, also described and has its usage. It is also instantly applicable in a production and cooling systems and it's resourceful.

COMPERATIVE ADVANTAGE OF INVENTIONS *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion* AND *The Formulation of Watery Solution of Inhibitor Against Corrosion for Utilized Antifreeze*:
Nontoxic liquids, biodegradable, and are not harmful for the environment, water, nature, human health, animals, pats and fishes.

STATE OF TECHNIQUE AND MARKET

THE INHIBITOR AGAINST CORROSION OF THE SYSTEM OF COOLING AND HEATING FOR THE UTILIZED FLUID – ANTIFREEZE IN AQUEOUS SOLUTION

The invention and a solution of the technology is the usage of concentrated inhibitor for the utilized antifreeze on nontoxic base. This is nontoxic inhibitor. Its especially advances is an efficiency, because, this inhibitor is added in a small quantities to the utilized antifreeze. This inhibitor has a big power. It regenerates utilized antifreeze, persists a high temperature of boiling, reduces freezing temperature and has a great power of anticorrosive protection of cooling and heating systems. The biggest advantage of this inhibitor is that it can be universal used in any antifreeze. It's

primarily purpose is for nontoxic antifreeze against freezing and corrosion (invention *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion*), but it also can be successfully used in any other antifreeze on toxic base, but then it doesn't have nontoxic meaning, but toxic, regarding to small quantity in no disintegrating antifreeze. The most significant accomplishment of this inhibitor is that it has been done with polycarboxylate, which formulation is disintegrated in alcohol, mix alcohol/water and in water. It doesn't corrode or violates cooling system, and it's effective in small quantities.

The goal of this invention is to provide formulations of concentrated inhibition of corrosion for diluted and utilized configuration of anti/ice antifreeze coolers with polymark poly-carboxylated additives, in configuration with other inhibitors which are used in this formulation, and have a great power of anticorrosive protection. This inhibitors are prerequisite for the invention *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion*, too. There isn't any similar or the same invention on domestic and foreign market.

INVENTION BASE is consists of the fact that the utilized antifreeze is modified and regenerated with a small quantity of the invention, stops the corrosion of engine, extends the life-time of antifreeze, increases freezing point and boiling point, brings alkali reserve to the satisfactory level and increases pH value.

1. Invention field

This invention is in relation to the formulation of aqueous corrosion inhibitor and especially to the corrosion formulation which can be added to the utilized composition of antifreeze / cooler on nontoxic base, on the multi atomicity alcohol (glycerol) or compositions which are not on this base.

2. Traditional fluids antifreeze/cooler became weaker during usage. Its time of duration and utilization is very limited. The fluid on nontoxic base, considering the quality of the base, is more persistent. They all used phosphate salts to help maintaining of stable alkali circle from which many corrosion inhibitors can be effective. There is a reduction of the pH value at utilized antifreeze and its protection from corrosion became minimal or there isn't any at all. Therefore by adding of small package of concentrated corrosion inhibitor we can achieve a high level of protection against corrosion. This formulation of corrosion inhibitor is designed, above all, for the modern cooling systems in passenger vehicles with aluminum engines, although it is successful for the all the cooling and heating systems. The formulation of this inhibitor is easy to mix with aqueous solution in diluted and utilized fluid in cooling system, has useful and long life, doesn't damage a color and reduces foam. This formulation of inhibitor greatly reduces a corrosion including aluminum and aluminum alloy, copper, brass, cast iron, steel, bronze and solder. This formulation has been done with polymark polycarboxylate additives which has extremely high level of protection from corrosion. The formulation of this inhibitor against corrosion is finally attested by modified method, ASTM method, DIN method.

The inhibitor is an anticorrosive protection of all cooling and heating systems, which is added in nontoxic antifreeze against freezing and boiling (invention *The*

Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion), and consists of several components. Successful combinations which are balanced for this kind of fluid – for the cooling and heating systems, as a anticorrosive protection, are inhibitor additives, which are improved, such as: benzo-three-azole, three-ethanol-amine, sodium-tetra-borate, three-ethil-amine, nitrate, sulfates, then inhibitor against corrosion in aqueous solution and in solution of alkali and salts, such as: ethanol-amine, potassium-chromate, sodium-nitrite, sodium three-poly-phosphate, di-ethanol-amine and sodium-benzoate. There is specially efficient an inhibitors in compounds, such as: three-ethanol-ammonium-phosphate, calcium meta-borate, sodium meta-borate, sodium nitrite. This inhibitors are applied in the form of solution concentration (a formula is not available to the public). The summary of the chemical compounds is not given with the chemical formulas. The summary of the technological composition is given under A and B.

TECHNICAL FIELD

According to international patent classification the invention is assorted in class C 09 K 005/00, by which the equipages and gadgets on vehicles are defined for the remission of cooling the machinery units by cooling liquid. The invention could be also assorted in class F 01 P 3/00 or in class V60K 11/02 by which the cooling of engine in general is defined, that is, cooling by cooling liquids.

Such as invention-patent isn't known on domestic market as well as on foreign market with such efficiency, as an inhibitor for utilized fluids, and for an inhibition of aqueous solution of anticorrosive protection in a new fluid.

This inventions has been done on nontoxic base.

That's why it's called Invention for 21st Century New technology

SOLUTION OF THE TECHNICAL AND PERFORMING PROBLEM

The technical problem is solved by mixing of several components of inhibitor against corrosion and by establishment of balance, and then by combining in one component it makes an unique inhibitor against corrosion in engine cooling system. The composition of these components is designed in a way which makes an inhibitor to be successful against corrosion in all systems of heating and cooling. This inhibitor is intended for all liquid solutions of fluid, for utilized fluids with very low inhibitor's protection, and it's intended for fluid inhibition in production of nontoxic antifreeze against freezing and corrosion (invention *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion*) and as modifier and regenerator of utilized fluids in longer exploitation. A very small quantity is added for modification, and for the manufacturing of nontoxic antifreeze, invention *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion* in prescribed proportion.

A technological process is performed in a following way: anticorrosive substances are mixed in one, first, those substances are dissolved in water or alcohol solutions, depends on substance, what is more dissoluble in what. Then, all components are combined in one according to author instruction, in a concentration

described in tables of this invention. A technological process is performed in a reactor (container) with heating and cooling and maintenance of constant temperature between 80-90°C. A mixing process, after warming up, lasts about one hour. In this process there is 20-40% of distilled water, 20-30% of propylene glycol, 10-20% of multi atomicity alcohol (glycerol), and the rest is a composition of inhibitor components. After that, there is a cooling of and filling in a specific package, according to market needs.

The biggest advantage of this invention is that an inhibitor's protection is advanced beside well balanced components of inhibitor protection, a poly-carboxylates, dissoluble in water or alcohol solution, are added (a mark is given in table "A").

An improved kind of stabile poly-carboxylate is based on poly-crilic acid or poly-maleine acid. These poly-carboxylates are in accordance with other components in production and exploitation of nontoxic antifreeze against freezing and corrosion (invention *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion*). The poly-carboxylates who could be used in this invention are those who are marked as BASF under the sign SOKALON®. These are poly-carboxylates who are available in water solutions. This inhibitor, marked as poly-carboxylate, can be mostly used in formulation from 0,01%-10%, but the most suitable is from 0,01%-0,1% (weight percent). This additive is best marked as SOKALON® CP-12S or CP-10. In this combination it's possible to use both kind of poly-carboxylate.

Formulation of inhibitor against corrosion in systems of cooling and heating for utilized fluid/antifreeze and the inhibitor for production of antifreeze against freezing and corrosion

This invention is the inhibitor for nontoxic antifreeze against freezing and corrosion (invention *The Formulation of Nontoxic Liquid watery Solution Against Freezing and Corrosion*), it's an integral substance of this antifreeze, biodegradable generation. This inhibitor is designed for usage as a modifier and regenerator for utilized antifreeze in order to extend its usage period and refresh anticorrosive protection of wide range of internal combustion engine and other engines, as well as cooling and heating systems, also including those who are produced by General Motors and Ford (America). This inhibitor is used in small quantities, for regeneration and modification of utilized antifreeze from 8-12% of weight in which it's purred, and for the antifreeze who has an inhibitor as a substance it's between 10-18%.

This inhibitor as a corrosion stopper is a formulation of addition for utilized fluid/anti-ice of nontoxic antifreeze against freezing and corrosion (invention *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion*).

The invention is usable instantly and a subject of its protection is a procedure, a composition and technological process.

Formulation of inhibitor of aqueous anticorrosive agent

B) Formulation of specific additives

1. Glycerol
   - chemical formula $C_3H_8O_3$
   - quality at least 98,0% (99,5%)

2. Water – soften or distilled

3. Benzotriazole who is an effective corrosion inhibitor of all variety of metals in neutral solutions.

4. Three-ethanol-amine (three-ethile-amine $(HOCH_2CH_2)_3N$ a corrosion inhibitor of iron and steel in water solutions.

5. Sodium-tetraborate
   - chemical formula $Na_2B_4O_7$
   - an inhibitor in composition of this formulation of several metals, aluminum and its alloys.

6. Sodium-three-polyphosphate
   - applied for the protection of circular systems as heater exchanger from 4°C till 99°C. It's efficient as the inhibitor in wide range of pH but not bellow 6. This additive isn't toxic.

7. Sodium-nitrate
   - chemical formula $NaNO_3$
   - in formula composition protects several metals

8. Sodium-nitrite
   - chemical formula $NaNO_2$
   - necessary concentration depends on conditions of corrosion and water composition in formulation.

9. Sodium-sulfide
   - chemical formula (without water Na_2SO_3) or $(Na_2SO_3)7H_2O$
   - in this formulation good corrosion inhibitor of magnesium, aluminum and its alloys in alkali environment and in water solution of glycerol.

10. Potassium-sulfide
   - chemical formula K_2SO_4
   - quality at least 99%
   - solution- easily soluble in water
   - in this formulation inhibitor of aluminum, magnesium or its alloys.

11. Sodium – meta-silicate
    - inhibitor corrosion of aluminum in water solution of this formula

12. Potassium-dichromate
    - this additives is used for metal protection in contact with antifreeze.

13. Sodium – chromate
    - chemical formula in acids HNO_3, H_3PO_4 i H_2SO_4
    - inhibitor of corrosion of steel, cast iron, aluminum, copper, zink, brass in water solution of this formulation

14. Sodium – benzoate
    - chemical formula $C_6H_5SO_6Na$ or ($C_7H_5O_2Na$)
    - inhibitor of corrosion of steel in water solutions and well maintained pH values and alkalis

15. Benzolsulphamide
    - chemical formula C6H5SO2NH2
    - inhibitor of corrosion of black metals
    - in this formulation also of other metals and their alloys

16. Calcium – cyanamide
    - in this formulation inhibitor of corrosion of steel in water solutions and salt solutions

17. Sodium-hydroxide
    - suitable for aluminum protection as well as for maintain of alkali reserve and pH-value between 9-11

18. Polimark-polycarboxilate BASF, soluble in water and alcohol solution. In this invention marked as SOKALON® CP-12S or CP-10. In this formulation the ABC COBLEX's policarboxilate in concentration is also applicable.

19. Silicate oil

The new thing in all this is that this concentrate is not toxic, has very high efficiency of inhibition protection in small quantities. The design of this inhibitor is so well balanced that high quality is achieved. This data in tables are given abstractly. The inventor of the patent kept the right to choose the best solution in combination and adjusted this kind of antifreeze (fluid-liquid), the modified version to ASTM, DIN and JUS.

In order to maintain pH value between 9,5-11, the silicates are used, which are very important for aluminum engines in a way of protection of aluminum parts of cooling system, as well as for maintain the alkali reserve in this fluid. The most important component in maintaining of pH value is sodium-hydroxide in solution 0,5-

10% mass weight. The silicates and silicates inhibitors in solutions of this cooling fluid are specially interesting for North America area.

The basic goal of this invention is that it's: nontoxic, well disintegrated, ecologically acceptable.

For the formulation of nontoxic inhibitor against corrosion and regenerator – modifier for utilized antifreeze, there is the following:

TABLE "B"

FORMULATION	A	B	C
Components (%)			
A)			
- multi-atomicity alcohol	82,95	75,65	63,55
- distilled water	5,00	5,00	5,00
- polimark-policarboxilate	1,0	1,30	1,60
- benzotriazole	1,0	2,20	4,20
- three-ethanol-ammine	0,80	1,10	1,60
- sodium-meta-silicate	0,20	0,40	0,90
-potassium-dichromate	0,30	0,70	1,10
B)			
- distilled water	5,00	5,00	5,00
- sodium-tetra-borate (borax)	0,30	0,45	0,90
- sodium-nitrate	0,35	0,40	0,70
- sodium-nitrite	0,20	0,45	0,60
- sodium-sulfide	0,30	0,90	2,20
- potassium-sulfide	0,25	0,40	1,20
- sodium-three-poly-phosphate	0,20	0,60	0,75
- sodium-chromate	0,20	0,45	1,20
- sodium-benzoate	0,30	0,85	1,20
- sodium-hydroxide	0,03	0,05	0,08
C)			
- benzol-sulfamide	0,30	0,45	1,00
- calcium-cyanamide	0,45	1,10	1,20
- silicate (silicate oil)	0,005	0,005	0,005

The way of performing the production process:

The components under A are mixing in water solution or in alcohol on 80-90°C with the components under B, which are added in mixed mass A, with mixing till the temperature of homogenization. Then, the components under C are added in the part of the mass. The color and silicon oil of 0,20% is added to this product. The sodium-hydroxide is specially prepared in water solution, after that, it's added to mixed mass. This composition of inhibitor is designed and done on the basis of long-term examinations and on the basis of the best expert opinion for this kind of product. Every change of the composition may result the instability of the product.

This product, the inhibitor and regenerator-modifier for the utilized antifreeze, is not toxic according to expert opinion of the Institute for chemistry in Belgrade as well as the Institute in Nürnberg, Germany, and it shouldn't be marked as toxic.

CONCLUSION

Beside the mentioned inhibitors, mono carbonic acid and poly-carboxylate in small concentration are very suitable for the corrosion inhibition of all various kind of engines. There are also azole compounds, suitable to this invention, including mercaptobenzothiazole, benzothiazole and poly-thiazole salts. The best are salts of nitrite and nitrate and their mixture. Phosphates can also be useful for the corrosion inhibition.

For this invention formulation of aqueous solution or concentrate, engine cooler or anti-ice, some of most suitable inhibitors were selected with well balanced inhibition, and protection for all kind of metals had been done. This technology has been done after intensive examination, and excellent results are obtained regarding protection of all mentioned kinds of metal.

The formulation is perfectly selected (review isn't given) but the balance is obtained on this base of aqueous engine cooler, as well as the concentrate.

The invention is finally attested by modified method in three X three method ASTM and DIN, using DIN method which has been used to estimate the invention formulation against corrosion. Beside that, corrosion standard test method on engine cooler in glass can with corrosive solution, has been used, too.

Invention examination by author is finished with this, and comparison with other conventional product for engine cooling, as well.

The result is: this is completely new technology ("new technology") and it hasn't been patented in the world till now.

The basic and the main goal of this invention is that it's: nontoxic, well disintegrating in water (biodegradable), ecological acceptable because it's not harmful to the environment and it doesn't pollute land, air and water. At the same time it's technological-technically improved, so it's useable in all cooling systems (cars), heating systems and in all heat transfer systems, as well as in the solar systems.

The inventions *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion* and *The Formulation of Watery Solution of Inhibitor Against Corrosion for Utilized Antifreeze* are designed and composed of different chemical substances so there are two dependent entirety. The first one is without inhibitor protection, and the second one is an inhibitor formulation for the first one as well as for the formulation of utilized fluid liquids in cooling and heating systems and in internal combustion engines.

With this formulation the tests had been and the cleaning procedure of metal sample had been performed by modified ASTM specification.

With prescribed temperature, 30-33% ASTM corrosive water. All the modifications are measured in milligrams corresponding to a standards.

Table 1

	allowed	obtained by measuring
cooper	5	-0.8
solder	10	+0.6
brass	10	-0.6
iron	5	+0.2
gray smelting	5	-2.4
aluminum	10	-5.0

The results from table 1 obtained by ASTM method are passing.

Analogue examination of corrosion

Corrosion: losses in weight of archetype coupons (mostly mg)

Table 2

	allowed	obtained by measuring
copper	5	-0.6
solder	10	+0.1
brass	10	-0.6
iron	5	+0.1
gray smelting	5	-2.3
aluminum	10	-5.9

The results are obtained by modified ASTM method. The results are passing.

Corrosion: losses in weight of archetype coupons, mostly mg (JUS H.Z8.O56)

Table 3

	allowed	obtained by measuring
copper	5	+1.9
solder	10	+1.8
brass	10	+2.7
iron	5	+3.4
gray smelting	5	+3.7
aluminum	10	+4.0

the results are obtained by analogue method according to JUS HZ8.O56 in glass can with corrosive liquid 30%, and antifreeze 1:1 for the temperature of –18°C PASS.

Analyses review

Which have been done in order to examine an anticorrosive protection, in better words a corrosion holder – nontoxic fluid/antifreeze against freezing and corrosion (invention *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion*) performed with an nontoxic inhibitor against corrosion for utilized antifreeze (invention *The Formulation of watery Solution of Inhibitor Against Corrosion for Utilized Antifreeze*).

3. examination by University in Novi Sad, Technical Science Faculty, a laboratory for physical-technical and solar measuring in 1988 and 1989. The results correspond to JUS, ASTM and DIN standards.
4. the extreme exploitation examinations has been performed for this formulation of fluid/antifreeze, in such a way that archetype coupons was cleaned according to ASTM method and specification. The archetype coupons were build in cooling system of General Motors's engines: Pontiac 2.300 cc, Pontiac 3.100 cc from 1991., Chevrolet Corsica 3.100 KW and Beretta 2.300 cc from 1991. The archetype coupons were used in exploitation of vehicle during summer and winter period on the temperature from –15°C till +35°C to 40°C. With such an examination between 5.000-20.000 km were passed, on the base of regular everyday drive.

On the base of this examination, the results in Tables 4,5,6 and 7 were obtained. Table 4, Corsica 3100 cc, passed 7.000 km; Table 5, Beretta 2300cc, passed 5.000 km; Table 6, Pontiac 2300 cc, passed 10.000 km; Table 7, Pontiac 3100cc passed 20.000 km. In all the vehicles the archetype coupons were built in for 8 months. The archetype coupons were built in cooling system on the highest gavitation pressure. For example, a working pressure of a water pump is about 1 kPa. Average working temperature in engine is about +110°C. After taking off, an archetype coupons were processed according to ASTM standard.

Achieved results shows that nontoxic antifreeze against freezing and corrosion (invention *The Formulation of Nontoxic Liquid Watery Solution Against Freezing and Corrosion*) with nontoxic inhibitor against corrosion for utilized antifreeze (invention *The Formulation of Watery Solution of Inhibitor Against Corrosion for Utilized Antifreeze*) meets high ASTM standard and it's a sufficient guarantee for all the engines in which this fluid/antifreeze is putting in a engine cooling system, and not only during the warranty period, but over 300.000 km or 6 years of engine exploitation.

Exploitation method

Table 4

	allowed	obtained by measuring
cooper	5	-1.2
solder	10	-2.4
brass	10	-0.2
iron	5	+0.6
gray smelting	5	+3.4
aluminum	10	+3.7

Table 5

	allowed	obtained by measuring
cooper	5	+1.2
solder	10	-2.3
brass	10	-2.4
iron	5	+0.4
gray smelting	5	-5.7
aluminum	10	+4.8

Table 6

	allowed	obtained by measuring
cooper	5	+2.4
solder	10	-0.5
brass	10	+0.6
iron	5	+1.4
gray smelting	5	+3.6
aluminum	10	+6.1

Table 7

	allowed	obtained by measuring
cooper	5	+1.9
solder	10	+1.8
brass	10	+2.0
iron	5	+8.6
gray smelting	5	+6.1
aluminum	10	+3.6

All the results meets a standards.